

1,036,354



# PATENT SPECIFICATION

1,036,354

Date of Application and filing Complete  
Specification: May 26, 1964.

No. 21709/64

Application made in Italy (No. 11691) on June 4, 1963.

Complete Specification Published: July 20, 1966.

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Index at Acceptance:—C2 C (1Q1A, 1Q6A1, 1Q8C, 1Q11B).

Int. Cl.:—C 07 c 17/08, C 07 c 19/08.

## COMPLETE SPECIFICATION

### NO DRAWINGS

### 1-Chloro-1-Fluoroethane

- We, MONTECATINI, SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, a body corporate organized and existing under the laws of Italy, of 1-2 Largo Guido, Donegani, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 The invention relates to a process for the preparation of 1-chloro-1-fluoro-ethane which is a useful intermediate for the synthesis of other fluorine-containing compounds.
- 15 In the process of the invention vinyl chloride is contacted with hydrofluoric acid in the liquid phase under atmospheric pressure, at a temperature of at most 30°C, and in the absence of a catalyst or in the presence
- 20 of an inorganic or organic acid catalyst. Preferably the vinyl chloride is continuously added in the gaseous state, into a liquid medium comprising anhydrous hydrofluoric acid, and then from the liquid phase
- 25 is continuously removed a gaseous stream comprising unconverted vinyl chloride a small amount of entrained hydrofluoric acid and an appreciable proportion of the addition product of the vinyl chloride and
- 30 hydrofluoric acid. The vinyl chloride is preferably continuously fed into a reaction vessel containing liquid anhydrous hydrofluoric acid at a temperature of from -15 to +19°C and
- 35 more preferably of from 0 to 15° C. From the reaction vessel in which, by means of known methods, a good contact between the gas and liquid can be achieved, a gas stream comprising 1-chloro-1-fluoro-ethane, unconverted vinyl chloride and entrained hydrofluoric acid, is removed continuously.
- 40 1-chloro-1-fluoro-ethane (b.p. 16.5°C) can be easily separated by distillation from vinyl

[Price 4s. 6d.]

chloride and hydrofluoric acid. The hydrofluoric acid can also be removed with ease 45 from the gases coming from the reactor by washing and absorption with water, or an alkaline solution.

According to another preferred process according to the invention higher reaction 50 rates between the vinyl chloride and liquid hydrofluoric acid are obtained under similar operating conditions and, as a result, greater conversions to fluoro-chloro-ethane, by adding to the anhydrous hydrofluoric acid, 55 an organic or inorganic acidic substance, such as sulphuric acid, oleum, sulphuric anhydride, phosphoric acid, phosphoric anhydride, perchloric acid, formic acid, acetic acid, trichloroacetic acid, and trifluoroacetic 60 acid as catalyst.

The catalyst can be present in an amount of from 0 to 50% by weight with respect to the hydrofluoric acid and is preferably present in an amount of from 5 to 25% by 65 weight.

Besides their catalytic activity these substances reduce the vapour pressure of hydrofluoric acid, and this makes it possible either to reduce the hydrofluoric acid content in the 70 gases coming from the reactor or to carry out the reaction at a temperature above the boiling point of hydrofluoric acid (19°C).

Under such conditions, the preferred reaction temperatures can vary for example 75 from -15 to +30°C.

The presence in the reactants of water in considerable amounts for example in proportions of more than 10% by weight with respect to the hydrofluoric acid, should be 80 avoided, since the presence of water may decelerate the addition reaction.

A certain amount of 1, 1-difluoro-ethane may be found in the reaction product. The formation of this product is particularly 85 surprising since hitherto the substitution of

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fluorine for another halogen atom at room temperature or below it, and even in the absence of particular catalysts, has not been thought possible. It has now been found 5 however, that the longer the contact time in the process of the invention the higher the proportion of 1, 1-difluoro-ethane in the gaseous product.

In general, the gaseous stream coming 10 from the reactor, which contains liquid hydrofluoric acid admixed or not with a catalyst or diluent, is made up of unreacted vinyl chloride, 1-chloro-1-fluoro-ethane, 1, 1-difluoro-ethane and entrained hydrofluoric 15 acid.

The composition of this mixture can be varied over wide limits depending upon the operating conditions, for example the vinyl chloride feed rate per unit volume of acidic 20 liquid phase, the presence and concentration of a catalyst, and the temperature at which the reaction zone is maintained, used.

In general, whether operating with or without a catalyst, it is suitable to have a 25 vinyl chloride flow rate of from 1 to 200 l/h (litres per hour) of gas per litre of liquid acidic phase. Under the preferred reaction conditions, at a temperature between  $-15$  and  $30^{\circ}\text{C}$ , the vinyl chloride is fed in an amount of from 10 to 100 l/h per litre of 30 acidic liquid phase.

By operating under such conditions once constant conditions are reached and the entrained hydrofluoric acid is eliminated, 1- 35 chloro-1-fluoro-ethane may be present in the effluent gases in an amount of from 5 to 95% by volume; and usually it is present in an amount of from 20 to 90% by volume.

In the same gases, 1, 1-difluoro-ethane can 40 be present in an amount of from 0 to 20% by volume; normally it is present in an amount of from 0.1 to 10% by volume.

The process of the invention is preferably carried out continuously.

45 According to a preferred embodiment, the vinyl chloride is fed in the gaseous state to the bottom of a reaction vessel, into which a liquid phase consisting of anhydrous hydrofluoric acid or a mixture of hydro- 50 fluoric acid and a catalyst has previously been introduced. The liquid contained in the reactor is maintained at the reaction temperature selected.

After a certain period of time, which is 55 usually rather short, the effluent gases may reach a constant composition which remains unaltered for quite a prolonged time.

The unreacted vinyl chloride can be easily separated, for example by distillation, from 60 the reaction product or products and recycled to the reaction zone. The hydrofluoric acid entrained by the gases coming from the reactor can be separated and recycled or removed by simple washing of the gases by 65 water or an alkaline solution.

Thy hydrofluoric acid consumed in the course of the reaction may be fed continuously to the reactor so as to keep the level of the liquid therein constant. If 70 needed, a continuous or periodical addition of the catalytic agent may advantageously be effected.

In order to raise the conversion of vinyl chloride an increase in the contact time 75 between the reactants can be provided by carrying out the reaction in a number of reactors arranged in series, thus increasing the residence time for the reactants.

The various reactors can be kept at 80 different temperatures and contain different concentrations of the catalytic agent and of hydrofluoric acid, so that the gaseous mixture has the optimum content of desired product and the lowest content of entrained hydro- 85 fluoric acid.

The invention will now be described in the following examples:

#### EXAMPLE 1

1.5 kg of anhydrous hydrofluoric acid are introduced into a reactor consisting of an 90 iron cylinder having an internal diameter of 12 cm and a capacity of 2.5 l, provided with a flanged cap having a gas inlet tube extending to 1 cm from the bottom, a gas outlet tube and a thermometer sheath. 95

While keeping the liquid at a temperature of  $0^{\circ}\text{C}$  by externally cooling the reactor with ice, 30 NI/h of dry vinyl chloride are continuously fed to the reactor.

The effluent gases are washed first with 100 water and then with a 10% KOH solution. After drying by passing them through a tower containing calcium chloride, the gases are condensed in a vessel and cooled to  $-78^{\circ}\text{C}$  by means of a dry ice methanol bath 105 applied externally.

After a period of about 3 hours, a sample of the effluent gases is analyzed prior to condensing, and was found to have a content of 38% by volume of 1-chloro-1-fluoro- 110 ethane and 2% of 1, 1-difluoro-ethane, the remainder consisting solely of unconverted vinyl chloride.

After 8 hours continuous operation, the content of 1, chloro-1, fluoro-ethane in the 115 gases coming from the reactor is found to be 39% by volume. Asymmetric difluoro-ethane is present in an amount of 3% by volume.

After a total of 8 hours operation, 680 g 120 of product having an average molar composition of 37.5% of 1-chloro-1-fluoro-ethane and 2.5% of 1, 1-difluoro-ethane, are condensed at a low temperature, and collected. The remainder consists exclusively of vinyl 125 chloride.

#### EXAMPLE 2

With the same equipment and following the same procedure as in example 1, with the exception that to 1.5 kg of hydrofluoric acid, 130

0.20 kg of 98%  $\text{H}_2\text{SO}_4$  are added at  $0^\circ\text{C}$ , once the conditions of normal operation are reached and the entrained hydrofluoric acid has been separated, the gas effluent from the reactor contains 53% by volume of 1-chloro-1-fluoro-ethane and 1.5% of asymmetric difluoro-ethane, the remained comprising vinyl chloride. The composition of the effluent gas remains practically unaltered over a further 15 hours of continuous operation.

The amount of hydrofluoric acid entrained by the gas stream coming from the reactor, under such conditions, is found to be reduced to about 1/3 of the amount in Example 1.

#### EXAMPLE 3

A run similar to the one described in Example 2 is carried out, with the exception that 50 NI/h of vinyl chloride, instead of 30 NI/h are fed to the reactor.

After about 1 hour, normal conditions being reached, a content of 44% by moles of 1-chloro-1-fluoro-ethane in the effluent gas is found.

#### EXAMPLE 4

This Example is carried out in the equipment used in Example 1. After introduction of 1.4 kg of anhydrous hydrofluoric acid and 0.40 kg of 98%  $\text{H}_2\text{SO}_4$ , 30 NI/h of vinyl chloride are fed to the reactor kept at  $18^\circ\text{C}$ .

After about half an hour, 1-chloro-1-fluoro-ethane is present in the effluent gases in a proportion of 63% by volume.

1, 1-difluoro-ethane is present in an amount of 4.5% by volume.

This composition remains practically unaltered after 15 hours reaction.

#### EXAMPLE 5

An iron vessel having an internal diameter of 13 cm and 10 l capacity, having a flanged cap carrying tubes extending to 2 cm from the bottom, for inlet of vinyl chloride and hydrofluoric acid, and a gas outlet, thermometer sheath and liquid internal level gauge, is employed.

1 kg of oleum containing 25% free  $\text{SO}_3$  and 5.5 kg of anhydrous hydrofluoric acid are introduced into the reactor. While keeping the acidic liquid mixture at a temperature of  $13$  to  $15^\circ\text{C}$ , 150 NI/h of anhydrous vinyl chloride are continuously fed to the reactor. The effluent gases are washed first with water and then with a 10% KOH solution, and then collected in a gas-holder.

After half an hour, 1-chloro-1-fluoro-ethane is present in the gases coming from the reactor in a proportion of 70% by volume, while 1, 1-difluoro-ethane is present in an amount of 2.5% by volume, the re-

mainder consisting exclusively of vinyl chloride.

Throughout this time the level of the liquid is kept constant by periodical additions of anhydrous hydrofluoric acid, after which time, the rate of vinyl chloride inlet is raised to 300 NI/h.

The average composition of the gas coming from the reactor is, after a very short period of time, 63% by volume of 1-chloro-1-fluoro-ethane and 2.3% by volume of 1, 1-difluoro-ethane.

This composition remains practically unaltered during a further 48 hours continuous operation, the level of the acidic mixture in the reactor being maintained constant by periodical additions of anhydrous hydrofluoric acid.

#### WHAT WE CLAIM IS:—

1. A process for the preparation of 1-chloro-1-fluoro-ethane in which vinyl chloride is contacted with hydrofluoric acid in the liquid phase under atmospheric pressure, at a temperature of at most  $30^\circ\text{C}$ , and in the absence of a catalyst or in the presence of an inorganic or organic acid catalyst.

2. A process according to Claim 1 in which the vinyl chloride is continuously added in the gaseous state, into a liquid medium comprising anhydrous hydrofluoric acid.

3. A process according to Claim 2 in which the reaction is carried out at a temperature of from  $-15$  to  $+19^\circ\text{C}$ .

4. A process according to Claim 1 in which gaseous vinyl chloride is continuously added to a liquid reaction medium comprising 100 parts by weight of anhydrous hydrofluoric acid and 0 to 50 parts by weight of an inorganic or organic acid as catalyst.

5. A process according to Claim 4 in which sulphuric acid or oleum is used as a catalyst.

6. A process according to any preceding Claim in which 10 to 100 NI/h of gaseous vinyl chloride are added per litre of acidic liquid mixture, at a temperature between  $-15^\circ$  and  $30^\circ\text{C}$ .

7. A process for the preparation of 1-chloro-1-fluoro-ethane as described in any of the foregoing Examples.

8. 1-chloro-1-fluoro-ethane prepared by a process as claimed in any preceding Claim.

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